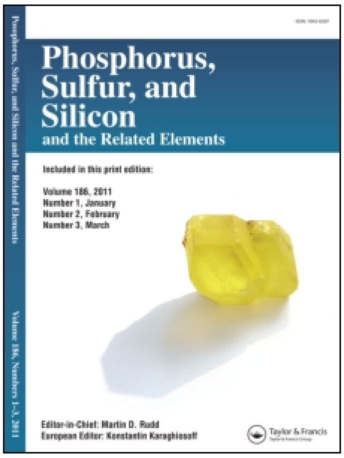

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Improvement of the Fe-NTA Sulfur Recovery System by the Addition of a Hydroxyl Radical Scavenger

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Improvement of the Fe-NTA Sulfur Recovery System by the Addition of a Hydroxyl Radical Scavenger

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The degradation of Nitrilotriacetic Acid (NTA), which results from the oxidation of hydroxyl radicals formed in the process, is a major deficiency in the present Fe-NTA system for the oxidation of hydrogen sulfide to sulfur by air. The degradation of NTA can be slowed down considerably by the addition of a hydroxyl radical scavenger. In this study, a series of inorganic and organic materials was tested as scavengers/inhibitors of hydroxyl radicals in attempts to improve the Fe-NTA system. The results showed that N-methylpyrrolidinone and ethylene glycol could be used as potentially powerful scavengers of hydroxyl radicals to improve the Fe-NTA system.

Keywords Ethylene glycol; Fe-NTA system; N-methylpyrrolidinone; scavenger of hydroxyl radicals

INTRODUCTION

Chelated-iron liquid-redox processes are increasingly employed in a variety of industries to concurrently absorb and oxidize the hydrogen sulfide component of gas streams to elemental sulfur.[1] In most cases, the catalysts used commercially are Fe(III)/Fe(II) chelates, and the chelating agent is an aminopolycarboxylic acid, such as Ethylenediaminetetraacetic Acid (EDTA), *N*-Hydroxyethylethylenediamine-*N*,*N'*,*N''*-Triacetic acid (HEDTA), or Nitrilotriacetic Acid (NTA).[2]

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Significant operating costs that are incurred in the process due to the oxidation and eventual loss of the ligand is a serious deficiency, which limits the use of this system in large installation for the removal of hydrogen sulfide by catalytic oxidation. It is generally recognized that the hydroxyl radicals formed in the reoxidation of Fe^{2+} with O_2 to Fe^{3+} and usually associated with a "Fentons Reagent" are responsible for the degradation of the ligand. The rate of degradation can be slowed down considerably by the addition of $Na_2S_2O_3$, which is known as a quite effective scavenger for the hydroxyl radicals. It has been found that $Na_2S_2O_3$ is beneficial at concentrations up to 0.5 M in protecting the Fe-NTA from degradation by hydroxyl radical attack. A higher concentration of thiosulfate provides little further improvement. On the contrary, further oxidation of $Na_2S_2O_3$ to sulfate via tetrathiosulfate results in inert salt accumulation, which eventually hampers the sulfur separation as well as the gas–liquid mass transfer in the process.

To circumvent the previously mentioned problem, we considered three approaches:[3] (i) to develop some alternative ligands that are more robust than NTA and would be resistant to hydroxyl radical attack,[4] (ii) to explore novel nonaqueous redox couple systems to replace the aqueous Fe-NTA system,[5] and (iii) to find more effective scavengers of the hydroxyl radicals than $Na_2S_2O_3$ to lengthen the lifetime of NTA.

Our previous work[3–5] has proved that it is very difficult, if not impossible, to find a better and more practical ligand than NTA. What is more, as reported by Hancock et al.[6] and Chen et al.[7] in their research on pyridine-type ligands, such as pyridine-2-phosphonic-6-carboxylic acid (2PP6C), 2,6-pyridine-diphosphonic acid (2,6-PDPA), pyridine-2,6-dicarboxylic acid (DIPIC), and 2-carboxy-8-hydroxyquinoline (CHOX), the absence of α-methylene groups, which are known to be easily subjected to attack and oxidation by free hydroxyl radicals, does not guarantee against the oxidative degradation of the ligands. Therefore, finding more effective scavengers of free hydroxyl radicals substituting $Na_2S_2O_3$ appears to be a preferred option for the currently commercial Fe-NTA system. Although there are numerous radical scavengers or antioxidants that are related or applied to biological processes, few can be used directly on pure chemical processes, and even less are suitable for the aqueous Fe-NTA system because traditional scavengers or inhibitors of free radicals, such as dibutylmethyl phenol, *N*-acetylcysteine, diisopropylphenol, allopurinol, indole-3-acetyl acid, butylalcohol, ascorbic acid, and quinolinic acid et al.[8–12] are either insoluble in aqueous solution or too expensive to be used in the process for the conversion of H_2S to sulfur. Ideally speaking, additives that not only remove the free radicals but also can be regenerated automatically in the system are the best choice; however, they are not always available.

Therefore, our screening was carried out using various reagents that could be oxidized by free hydroxyl radicals. As long as efficiency, cost, and environmental factors are acceptable, it is worthwhile even if the additives were consumed sacrificially for NTA. With this in mind, we tested inorganic and organic compounds as scavengers or inhibitors of hydroxyl radicals for the Fe-NTA system. The results are compared with that of $Na_2S_2O_3$ concerning the half-life time of NTA, the selectivity to sulfur, the loss of Fe ions, and so on.

The following inorganic and organic compounds were screened: potassium iodide (KI), potassium bromide (KBr), potassium chloride (KCl), ammonium thiocyanate (NH_4SCN), sodium nitrite ($NaNO_2$), dimethylsulfoxide (DMSO), sorbitol, *N*, *N*-dimethylacetamide (DMAA), hexamethylenetetraamine (HMTA), triethanolamine (TEA), ethanolamine (EA), 1,3,5-tris(2-hydroxyethyl)hexahydro-[1,3,5]-triazine (THHT), ethylene glycol (EG), polyethylene glycol (PEG), glyoxylic acid (GA), glycerol, glyoxal, acrylamide, furan, and *N*-methylpyrrolidinone (NMP).

RESULTS AND DISCUSSION

General Screening of Scavengers

All the previously discussed compounds are found to be able to diminish radical-induced oxidative degradation of NTA to some extent. Among them, potassium halides KCl, KBr, and KI are the simplest examples. The addition of KCl, KBr, and KI to the Fe-NTA system gave a four- to ninefold increase in the half-life time of NTA (Figure 1a and Table I)

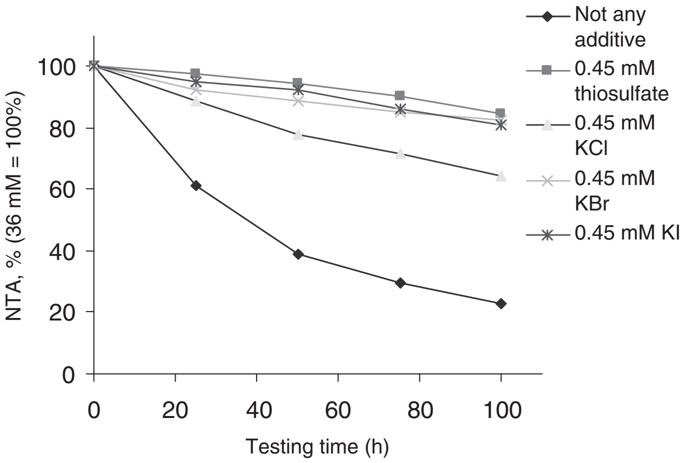


FIGURE 1a The degradation of NTA in the Fe(III)-NTA system with and without an additive under comparable conditions.

TABLE I Catalytic Activities of the Fe-NTA System With Various Scavengers

Scavenger	Conc.	Test Time (h)	Consumed NaOH (2N)	H_2S to Sulfur (%)	H_2S to $S_2O_3^{2-}$ (%)	H_2S to SO_4^{2-} (%)	Loss of Fe (mg/L/h)	Half-Life time of NTA (h)
None	0	100	43	92.8	1.8	5.4	0.8	39.9
Cl^-	0.45 M	95	28	96.6	2.2	1.2	1.3	154.0
Br^-	0.45 M	95	29	96.8	2.3	0.9	0.4	367.5
I^-	0.45 M	100	31	95.8	1.8	1.5	0.6	331.7
$Na_2S_2O_3$	0.45 M	96	37	114.2[a]	*	*	0.7	417.6
NH_4SCN	0.45 M	95	64	86.1	5.0	8.9	0.7	415.7
$NaNO_2$	0.45 M	95	38	84.9	2.2	12.9	10.5	617.2
DMSO	0.45 M	95	58	97.8	0.7	1.5	0.6	560.7
HATH	0.45 M	102	24	90.7	7.9	1.5	3.5	145.8
TEA	2 %	96	44	91.3	7.7	0.6	0.3	260.6
EA	2 %	96	58	92.9	6.1	1.0	0.9	204.7
DMAA	5 %	96	38	88.7	10.5	0.8	0.3	647.8
THHT	2 %	98	44	88.4	9.4	2.1	1.8	119.0
Furan	2 %	96	32	91.8	7.4	0.9	0.5	198.0
Acrylamide	2 %	96	42	93.7	6.0	0.4	0.5	306.0

[a] Including that produced from $Na_2S_2O_3$ and a calculation based on consumed H_2S.

*Difficult to calculate.

compared with the system without any additives (ca. 40 h). The function of Cl^-, Br^-, or I^- as a radical scavenger in the process could be interpreted from the following mechanism: the X^- anion reacted with the hydroxyl radicals to yield Cl_2^-, Br_2^-, and I_2^- radicals; the latter then are reduced by Fe(II)-NTA to regenerate Cl^-, Br^-, and I^-. The halides, however, were not as good as $Na_2S_2O_3$ in both extending the half-life time of NTA and yielding sulfur. When $Na_2S_2O_3$ was used, there was 14% of extra sulfur formed over the calculated yield due to the decomposition of $Na_2S_2O_3$.

$$2X^- + OH \longrightarrow X_2{\bullet}^- + OH^- \tag{1}$$

$$X_2{\bullet}^- + Fe(II)NTA^- \longrightarrow 2X^- + Fe(III)NTA$$

$$X = Cl, Br, \text{ and } I$$

As shown in Figures 1b–1d and Table I, even more dramatically different effects can be achieved with ammonium thiocyanate (NH_4SCN), sodium nitrite ($NaNO_2$), DMSO, DMAA, HMTA, TEA, EA, THHT, acrylamide, and furan.

The effect of NH_4SCN on enhancing the half-life time of NTA is similar to that of $Na_2S_2O_3$. However, a low yield of sulfur (86.1%) and a relatively high yield of side products (up to 14%) were found in this system. The decomposition of NH_4SCN was also obvious in the process.

$NaNO_2$ is not only a gentle reducing agent but also a gentle oxidizing agent in aqueous solution. The application of $NaNO_2$ to the Fe-NTA system increased the half-life time of NTA to 617.2 h, suggesting the

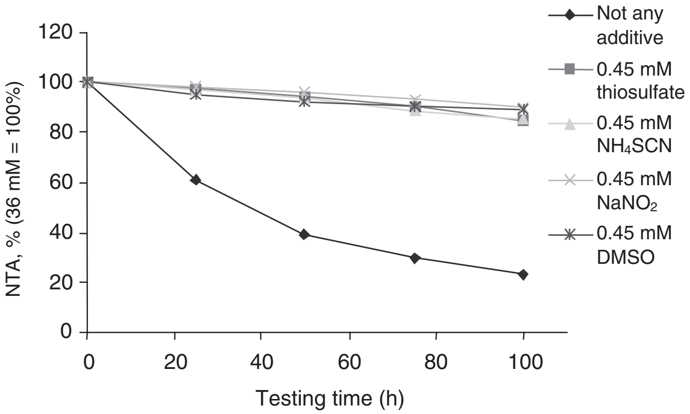


FIGURE 1b The degradation of NTA in the Fe(III)-NTA system with and without an additive under comparable conditions.

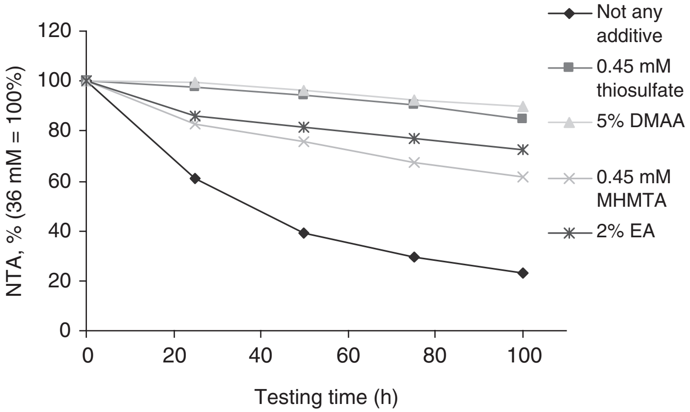


FIGURE 1c The degradation of NTA in the Fe(III)-NTA system with and without an additive under comparable conditions.

reducing function works to react with free hydroxyl radicals in the process as expected. However, the yield of sulfur (84.9%) was not satisfactory. The concentration of SO_4^{2-} (up to 12.9% in the resulting solution) was quite high, implying the action of the oxidative property of $NaNO_2$. In addition, a severe loss of iron was also observed in this system.

With the ideal conversion of H_2S to sulfur (97.8%), the satisfactory half-life time of NTA (560.7 h), and low formation of side products, DMSO seems a better scavenger of hydroxyl radicals for the Fe-NTA system than $Na_2S_2O_3$. The high consumption of NaOH (2 M) (up to

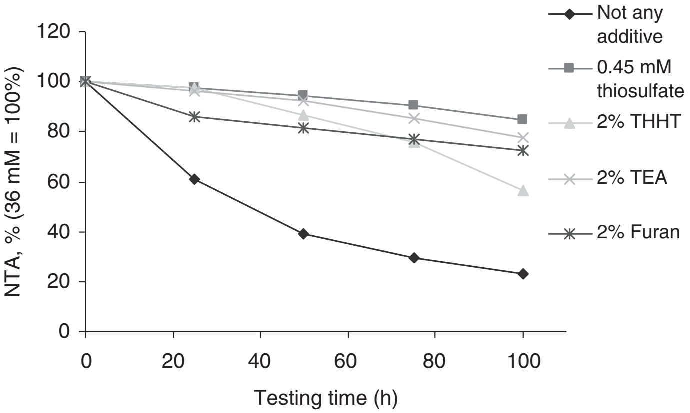


FIGURE 1d The degradation of NTA in the Fe(III)-NTA system with and without an additive under comparable conditions.

58 cm^3 for 95 h running) means, however, that DMSO was oxidized very rapidly by O_2 or the hydroxyl radicals in the process. In addition, during the process, a malodorous smell was released due to the formation of methyl sulfone (the oxidized product of DMSO), which limited its application as a scavenger of hydroxyl radicals for the Fe-NTA system.

DMAA was found to be somewhat more effective in enhancing the half-life time of NTA than $Na_2S_2O_3$. The lower conversion of hydrogen sulfide to sulfur (only 88.8%), however, proves that it is not the ideal scavenger for the Fe-NTA system either.

TEA reacted with Fe(III) or Fe(II) ions to form stable iron complexes, which could prevent the precipitation of iron hydroxide at up to pH 14. The introduction of TEA to the Fe-NTA system led to little loss of iron in the process. However, only a limited effect was found with TEA in extending the half-life time of NTA (260 h). The conversion of H_2S to sulfur (91.3%) was not marked. TEA functions as a stabilizer for Fe(III) and Fe(II) ions better than a scavenger of hydroxyl radicals for the Fe-NTA system.

When EA was added, the same selectivity to sulfur and a shorter half-life time of NTA than that with TEA were observed. However, a marked consumption of NaOH (2 N) (58 cm^3 for the 96 h running) and the extensive black solid precipitated out the outlet of H_2S in the Fe-NTA-EA system suggests that EA is not as good as TEA.

THHT was obviously unsuitable for improving the Fe-NTA system. Although the half-life time of NTA (119 h) is increased somewhat, the conversion of H_2S to sulfur (88.4%) was quite low due to the formation of further oxidized products. The loss of iron (up to 1.77 mg/L/h) was also remarkable.

The addition of acrylamide extended the half-life time of NTA to 306 h. The conversion of H_2S to sulfur was not bad (93.7%). However, the accumulation of a dark solid at the outlet of H_2S suggested that the Fe-NTA-acryl amide system was not stable enough. Acryl amide seems to decompose easily in alkaline solution. The presence of furan in the Fe-NTA system did not improve the lifetime of NTA. The half-life time of NTA is only 198 h. The less impressive conversion of H_2S to sulfur (91.8%) and the relatively high concentration of by-products mean that furan is not suitable as a scavenger of hydroxyl radicals for the Fe-NTA system for the catalytic oxidation of H_2S by air.

HMTA did not enhance the lifetime of NTA (146 h) much longer either. The marked loss rate of Fe ions (up to 3.35 mg/L/h) and the relatively low conversion of H_2S to sulfur (90.7%) also preclude the possibility for HMTA to replace $Na_2S_2O_3$ as a hydroxyl radical scavenger in the Fe-NTA system.

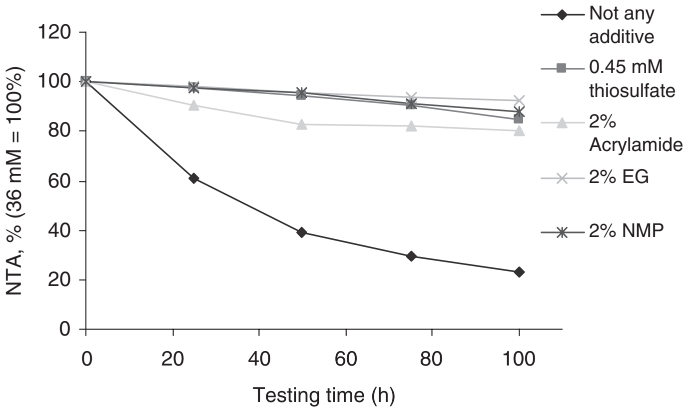


FIGURE 1e The degradation of NTA in the Fe(III)-NTA system with and without an additive under comparable conditions.

So far, none of the previously discussed reagents are as effective as $Na_2S_2O_3$ in extending the half-life time of NTA and increasing the selectivity to sulfur. The thiosulfate anion seems irreplaceable in stabilizing the NTA ligand in Fe-NTA system.

However, the effect of $Na_2S_2O_3$ was exceeded surprisingly by two cheap and simple compounds, EG and NMP. As shown in Figure 1e and Table II, the effect of EG and NMP on extending the half-life time of NTA was so strong that the half-life time of NTA was increased by at least an order of magnitude. Furthermore, Fe-NTA systems with EG or NMP showed good to excellent selectivity to sulfur. EG is thought to afford the most remarkable results, with sulfur yielding ≥99% and the longest half-life time of NTA (about 30 times as the original Fe-NTA

TABLE II Catalytic Activities of the Fe-NTA System With 2% EG and 2% NMP as Scavenger

Scavenger	EG	NMP	$Na_2S_2O_3$
Added amount (%)	2	2	6.3
Test time (h)	96	96	96
Consumed NaOH (2 N) (cm^3)	44	36	37
H_2S to sulfur (%)	99.4	97.0	114.2[a]
H_2S to $S_2O_3^{2-}$ (%)	0.3	2.2	*
H_2S to SO_4^{2-} (%)	0.3	0.8	*
Loss of Fe (mg/L/h)	0.5	0.6	0.7
Half-life time of NTA (h)	875.4	518.2	417.6

[a] Including that produced from $Na_2S_2O_3$ and a calculation based on consumed H_2S.
*Difficult to calculate.

system). No tail gas was evolved, and only a trace amount of byproducts and a moderate loss of iron ions were observed in this system. As will be described in the following section, the optimum concentration (20%) of EG in the Fe-NTA system made the degradation of NTA negligible. EG proved to be the most powerful hydroxyl radical scavenger for the conversion of H_2S to sulfur by air in the Fe-NTA system to date.

Influence of Concentration on the Efficiency of the Scavenger

As previously described, various additives show different effects in improving the Fe-NTA system. Even for the same additive (for instance, TEA), different activity was observed at different concentrations (Table I). EG and NMP at a 2% concentration show a much better effect than $Na_2S_2O_3$ (0.45 M or 6.3%). Is it possible to lengthen the half-life time of NTA and improve the selectivity to sulfur further by increasing the concentration of the additives? Experiments with NMP and EG proved that increasing the concentration of an additive within a certain range does improve the performance of the Fe-NTA system; however, a further increase of the concentration of EG and NTA is not really beneficial.

First, the maximum solubility of NMP in the aqueous Fe-NTA system was measured. A massive brown solid immediately precipitated out when the concentration of NMP was beyond 30 w/v %. A brown precipitate was formed gradually with the Fe-NTA solution consisting of 20–30 w/v % of NMP while stored at r.t. for more than a month. Therefore, the addition of NMP to the Fe-NTA system was limited below 20 w/v %. Table III and Figure 2 display the results with different concentrations of NMP. The conversion of H_2S to sulfur and the half-life time of NTA are found to increase with an increase of NMP concentration. The half-life time increases with an increase of the concentration of NMP

TABLE III Catalytic Activities of the Fe-NTA System With Various Concentrations of NMP Under the Same Conditions

Added concentration (%)	1	2	5	20
Test time (h)	96	96	100	98
Consumed NaOH (2 N) (cm^3)	36	36	39	30
H_2S to sulfur (%)	96.7	97.0	98.6	99.1
H_2S to $S_2O_3^{2-}$ (%)	2.4	2.2	0.7	0.6
H_2S to SO_4^{2-} (%)	0.9	0.8	0.7	0.2
Loss of Fe (mg/L/h)	0.9	0.6	0.1	0.3
Half-life of NTA (h)	387.5	518.2	852.6	823.6

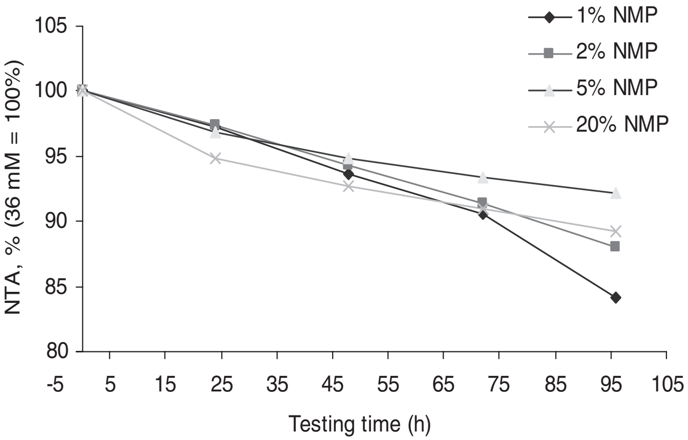


FIGURE 2 The degradation curves of NTA in the Fe(III)-NTA system with 1%, 2%, 5%, and 20% NMP under comparable conditions.

from 0 to 5 w/v %. However, a further increase of the concentration of NMP does not improve the half-life time of NTA (Figure 3).

EG is almost completely soluble (up to 95%) in aqueous Fe-NTA (pH 8.5–9.0) to give a stable homogeneous solution. As can be seen in Figure 4 and Table IV, in the range 1–20 %, the increase of the concentration of EG increasingly extends the half-life time of NTA. At the optimum concentration (20% of EG), the degradation of NTA is negligible. However, if the concentration of EG is beyond 20%, the half-life time of NTA is found to decrease with the increase of concentration of EG. The use of highly concentrated EG-Fe-NTA (EG concentration up to 95%) was even less effective than 2% of EG.

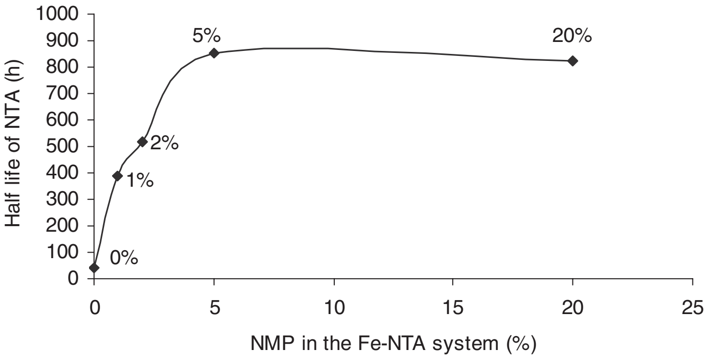


FIGURE 3 Half-life time of NTA with various concentrations of NMP in the Fe-NTA (test time: 96 h).

TABLE IV Catalytic Activities of the Fe-NTA System With Various Concentrations of EG

Added concentration (%)	1	2	5	10	20	50	95
Test time (h)	96	96	98	96	96	166	208
Consumed NaOH (2 N) (cm^3)	34	44	55	50	21	143	72
H_2S to sulfur (%)	93.9	97.3	99.2	95.3	93.6	94.5	96.5
H_2S to $S_2O_3^{2-}$ (%)	5.5	2.4	0.6	3.8	5.3	4.9	2.5
H_2S to SO_4^{2-} (%)	0.6	0.3	0.2	0.9	1.3	0.7	1.0
Loss of Fe (mg/L/h)	0.9	0.5	0.6	0.1	0.2	0.5	0.3
Half-life time of NTA (h)	424	875	1320	1459	26583	867	630

Proposed Mechanisms of NMP and EG in Removing the Hydroxyl Radicals in the Fe-NTA System

It has been shown that many additives, inorganic or organic, can decrease the degradation of NTA to some extent. This may result from the competitive reaction of the free hydroxyl radicals with the additive and with NTA or Fe-NTA. The additives can be either permanently decomposed/consumed/regenerated from the system or, more commonly, partly consumed and partly regenerated. Schemes 1 and 2 show the possible mechanism of NMP in removing the free hydroxyl radicals and the possible degradation products of NMP, respectively. In Schemes 3 and 4, the possible pathway of the reaction of free hydroxyl

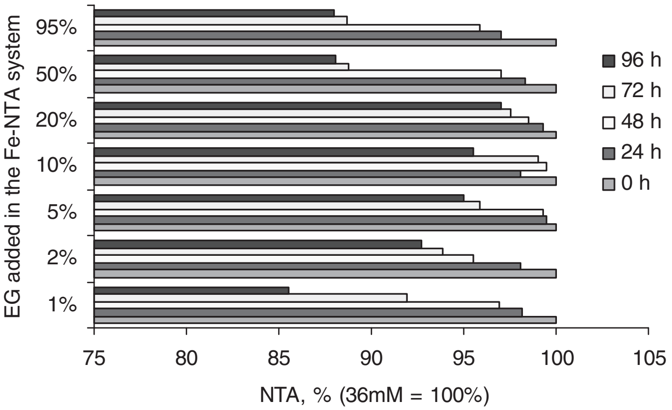
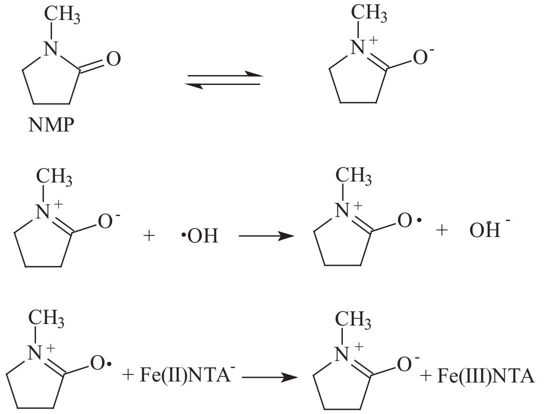


FIGURE 4 Degradation of NTA in the Fe(III)-NTA system in the presence of different amounts of EG with testing time under comparable conditions.

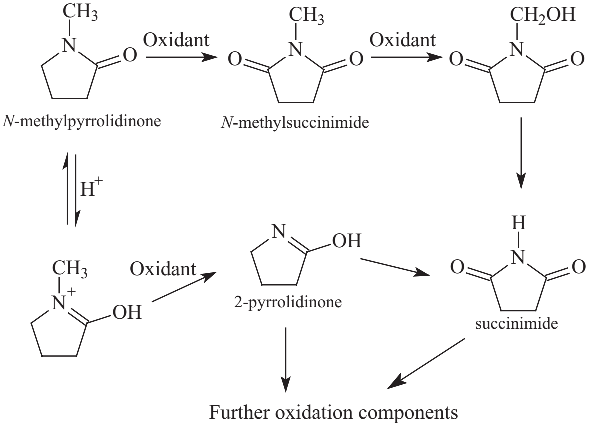


SCHEME 1 Suggested mechanism of scavenging hydroxyl radicals by NMP.

radicals with EG and corresponding decomposition compounds are displayed. However, it is not easy to find detailed evidence in such a complicated system, which consists of many components, including Fe(III)/Fe(II), NTA, and the scavenger itself, as well as the degradation products.

Function of NMP in Scavenging of Free Hydroxyl Radicals

NMP has been used to replace more volatile and toxic organic solvents in paint coating and cleaning applications. NMP-contaminated process water was oxidized harshly with ozone and hydrogen peroxide



SCHEME 2 Proposed oxidation pathway of NMP.

$$HOCH_2CH_2OH \rightleftharpoons HOCH_2CH_2O^- + H^+$$

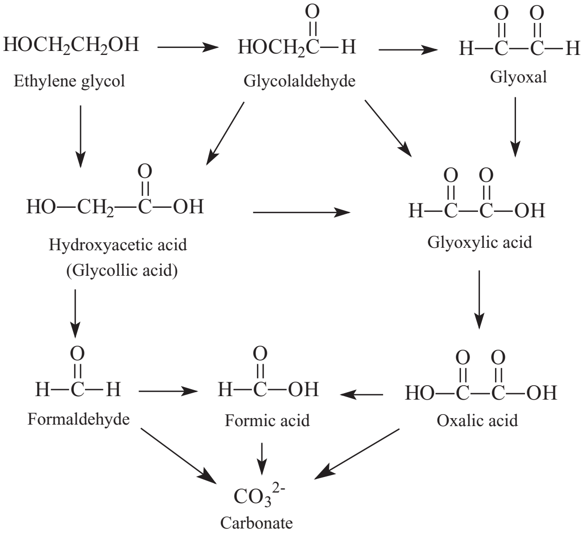
$$HOCH_2CH_2O^- + \cdot OH \longrightarrow HOCH_2CH_2O\cdot + OH^-$$

$$HOCH_2CH_2O\cdot + Fe(II)NTA^- \longrightarrow HOCH_2CH_2O^- + Fe(III)NTA$$

SCHEME 3 Suggested mechanism of scavenging hydroxyl radicals by EG.

in a semicontinous advanced oxidation reactor to reduce the organic concentration.[13] The oxidative byproducts of NMP were identified by GC/MS as methylsuccinimide, succinimide, 2-pyrrolidione, and acetaldehyde. The oxidation of H_2S to S by air catalyzed by a Fe-NTA-NMP system, though far milder than the O_3/H_2O_2 process, would also lead to a similar degradation of NMP as a consequence of a free hydroxyl radical attack (Scheme 2). We successfully monitored the concentration change of NMP in the absorption–oxidation process when NMP was used as scavenger of a Fe-NTA system and detected the decomposition product *N*-methylsuccinimide by HPLC (Table V). However, other degradation components of NMP, if there were any as shown in Scheme 2, were not found using this method.

As determined by HPLC (Table V), NMP is consumed to some extent in the process. The consumption of NMP is proportional to the starting



SCHEME 4 Proposed oxidation pathway of EG.

TABLE V Concentration of NMP and Its Oxidation Components in the Fe-NTA-NMP System

Concentration of NMP (%)	1	2	5	20
Concentration of NMP of the starting solution (g/L)	10.105	20.252	49.619	196.451
Concentration of NMP of the resulting solution (g/L)	9.640	19.092	45.382	167.200
The difference of the concentration, ΔC (g/L)	0.462	1.160	4.237	29.251
The loss of NMP (g/L/h) $\times 10^{-2}$	0.48	1.21	4.32	30.47
Concentration of NMS of the resulting solution (g/L)	0.283	0.763	3.902	5.752

concentration of NMP, while the accumulation of *N*-methylsuccinimide (NMS) is proportional to the consumption of NMP. For all experiments with NMP as an additive to the Fe-NTA system, the presumed oxidation product CO_3^{2-} has not been found in the resulting solution by the gravity method. This means that NMP degrades rather slowly through NMS etc. during the process. It may also be possible that NMP is regenerated in the process subsequent to reacting with scavenge radicals (Scheme 2). The effective performance of NMP in extending the half-life time of NTA suggests that NMP may be more vulnerable to the attack of free hydroxyl radicals or other oxidants than NTA.

Similarly, when we monitored the degradation of the Fe-NTA-EG system by HPLC, no carbonate was found in the resulting solution (Table VI). The concentration of oxalate, the actually ultimate degradation product, in the resulting solution (0.04–1.33 g/L) increased with the initial concentration of EG in the range 0–5%. The total degradation of EG proceeded more slowly when the initial concentration of EG reached up to 10%. The formation of the ultimate degradation product oxalate tended to decrease.

The absence of evidence of other intermediates did not affect our understanding that most of the intermediates of EG degradation are still oxidizable and can also function as a hydroxyl radical scavenger, making EG particularly effective in removing or inhibiting the free hydroxyl radicals in the Fe-NTA system. To confirm our assumption, comparative experiments were carried out with GA and glyoxal (Table VII), which are the supposed degradation intermediates of EG in the Fe-NTA system.

TABLE VI Concentrations of Oxalate in the Resulting Solution of the Fe-NTA-EG System (Test Time: 96 h)

Concentration of EG (%)	0	1	2	5	10	50
Concentration of oxalate (g/L)	0.04	0.79	0.82	1.33	0.78	0.53

TABLE VII Catalytic Activities of the Possible Degradation Products of EG: Glyoxylic Acid (GA), Glyoxal, and EG as Scavenger Under the Same Conditions

Scavenger	EG	Glyoxal	Glyoxylic acid
Added concentration (%)	2	2	2
Test time (h)	96	96	96
Consumed NaOH (2 N) (cm^3)	44	211	51
H_2S to sulfur (%)	97.3	87.4	92.7
H_2S to $S_2O_3^{2-}$ (%)	2.4	11.8	6.3
H_2S to SO_4^{2-} (%)	0.3	0.8	1.1
Loss of Fe (mg/L/h)	0.5	0.5	0.2
Half-life of NTA (h)	875.4	273.9	739.0

It turns out that both glyoxylic acid and glyoxal are effective in extending the half-life time of NTA. Glyoxylic acid not only gives comparable results with EG on the half-life time of NTA and a reasonable yield of sulfur but also leads to less loss of an iron ion than EG. Even so, it is still not economical to use glyoxylic acid as an additive commercially because glyoxylic acid is much more expensive than EG. However, the results support our proposal: the overriding effect of EG in extending the half-life time of NTA not only arises from itself (Scheme 3) but also from its successive oxidation derivatives (Scheme 4), which also show appreciable activity toward the free hydroxyl radicals.

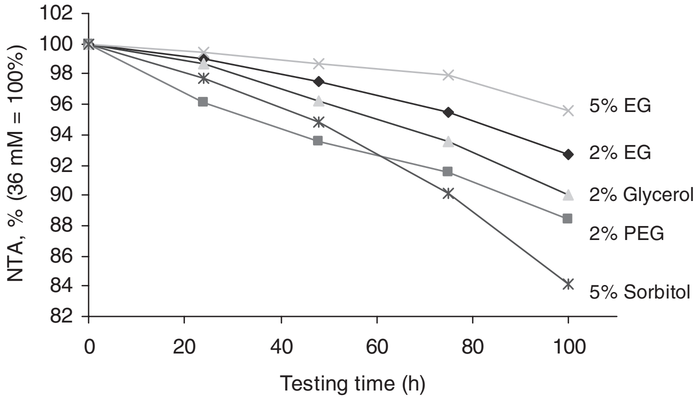


FIGURE 5 Comparative degradation of NTA in the Fe(III)-NTA system with EG, PEG, glycerol, and sorbitol as Scavenger under the same conditions.

TABLE VIII Catalytic Activities of Fe-NTA With the Analogues of EG as Scavenger

Scavenger	EG	Glycerol	PEG	EG	Sorbitol
Added concentration (%)	2	2	2	5	5
Test time (h)	96	96	96	98	96
Consumed NaOH (2 N) (cm^3)	44	58	69	55	53
H_2S to sulfur (%)	97.3	93.4	93.1	99.2	92.8
H_2S to $S_2O_3^{2-}$ (%)	2.4	6.3	6.4	0.6	6.6
H_2S to SO_4^{2-} (%)	0.3	0.3	0.5	0.2	0.6
Loss of Fe (mg/L/h)	0.5	0.7	0.3	0.6	0.2
Half life time of NTA (h)	875	630	539	1320	380

Comparative Studies of the Analogs of EG

Sorbitol is able to form a number of stable complexes with transition-metal ions including Fe(III) and Fe(II) by displacement of the protons from the hydroxyl groups of the ligand.[14–16] The excellent performance of sorbitol in stabilizing the Fe(III)/Fe(II) ion in basic conditions and its structural similarity to EG (with multi-hydroxyl groups) prompted us to consider it as both an iron stablizer and a scavenger of the free hydroxyl radicals at the same time in the Fe-NTA system. The addition of 5% of sorbitol did have a further effect in stabilizing the Fe(III)/Fe(II) ions, leading to the least loss of iron among all the related experiments. The selectivity to sulfur is good (94.9%). The half-life time of NTA (385.1 h), however, is slightly shorter than when $Na_2S_2O_3$ was employed. Obviously, sorbitol behaves better as a Fe(III)/Fe(II) stabilizer than as a scavenger of hydroxyl radicals.

PEG and glycerol, which are closer analogues of EG in structure than sorbitol, were also tested (Figure 5 and Table VIII). PEG and glycerol were found to be more effective than $Na_2S_2O_3$ at the concentration of 2% but less efficient than EG in extending the half-life time of NTA (539 h and 630 h respectively). An increase of concentration of PEG to 5% did not increase the half-life time of NTA (316.5 h) further.

CONCLUSIONS

A series of inorganic and organic compounds were tested as scavengers or inhibitors of hydroxyl radicals for the Fe-NTA system. Among them, NMP and EG were found to be more effective than $Na_2S_2O_3$. EG appeared to be a promising alternative of $Na_2S_2O_3$ for the current Fe-NTA system. In the ideal instance of Fe-NTA with 20% of EG, the degradation of NTA is negligible. The mechanisms of EG and NMP in scavengering free hydroxyl radicals and their possible degradation pathways have been proposed.

The analogs of EG, including glycerol, PEG, and sorbitol, were also tested as free hydroxyl radical scavengers for the Fe-NTA system. These additives, generally speaking, are better than $Na_2S_2O_3$ but are less effective than EG in improving the Fe-NTA system.

EXPERIMENTAL

Materials and Reagents

All materials and solvents were ordered from Aldrich or Lancaster and used without further purification. 1,3,5-tris(2-hydroxyethyl)-hexahydro-[1,3,5]-triamine THHT (99.0%) was provided by U.S. Filter and used directly.

Testing of the Activity of the Scavenger

Unless otherwise stated, all experiments were performed at conditions of pH = 8.50, H_2S flow rate = 2.00 cm^3/min, air flow rate = 700 cm^3/min, circulation rate of absorption solution = 100 cm^3/min, [NTA] = 36 mM, and [Fe(III)] = 18 mM.

To the oxidizer compartment of a one-liter reactor[3] was added the aqueous Fe(III)-NTA solution with an appropriate amount of a scavenger of hydroxyl radicals at pH 8.5. The liquid pump was then started, and some of the solution was pumped into the absorber compartment with a flow rate of 100 $cm^3\ min^{-1}$. The pH and redox probes were then turned on. At this stage, the air was bubbled into the oxidizer, and the air flow rate was adjusted to the required value. The valve of the H_2S cylinder was switched on, and the H_2S flow rate was adjusted to 2.00 $cm^3\ min^{-1}$. The starting time of the reaction was recorded, and the pH and redox probe readings were recorded from time to time. The pH was continuously kept to 8.50 by the addition of 2 M of NaOH solution with a syringe pump. The sulfur was filtered off with every ca. 24 h intervals, and a 5-cm^3 sample was taken from the running system every 24 h in order to monitor the degradation of NTA and the loss of iron.

HPLC Analysis

A Milton Roy Pump No. 043 024 equipped with a chromatography accessory, UV-visible spectrometer 3000 (LDC analytical), and a chart recorder (Waters 746 Dato Module) was used.

Analytical column: Spherisorb ODS II 5 μm 4.6 mm × 250 mm; column mobile phase; acetonitrile:water = 5:95; flow rate: 1.0 $\text{cm}^3\text{min}^{-1}$; temperature: ambient; detector: UV absorption at 220 nm; injection sample: 10 μL; recorder: 10 mV full scale; chart speed: 0.5 cm min^{-1}.

0.04 g of the reaction mixture was taken from the oxidizer compartment of the one-liter continuous reactor and placed in a 100-cm^3 volumetric flask. This sample was diluted to 100 cm^3 with water and then passed through a 0.45-μm filter before analysis.

Quantitative analyses of NMP and its degradation intermediates were based on the calibration curve established by varying the concentration of the corresponding known samples. Peak heights at the indicated amplification settings were plotted vs. the concentration of the species. The linear nature of these plots indicated precise HPLC determinations of these molecular species over a considerable range of concentration.

REFERENCES

[1] G. X. Hua, D. McManus, and J. D. Woollins, *Comments Inorg. Chem.*, **22,** 327 (2001).

[2] D. McManus and F. R. Kin, *US Patent,* **4,** 622,212 (1986).

[3] G. X. Hua, PhD Thesis, University of St. Andrews, UK. (2003).

[4] G. X. Hua, Q. Z. Zhang, D. McManus, A. M. Z. Slawin, and J. D. Woollins, *Main Group Chemistry*, **4,** 157 (2005).

[5] G. X. Hua, Q. Z. Zhang, D. McManus, A. M. Z. Slawin, and J. D. Woollins, *J. Chem. Soc., Dalton Trans.*, 1147 (2006).

[6] R. D. Hancock, A. E. Martell, and D. Chen, *Can. J. Chem.*, **75,** 591 (1997).

[7] D. Chen, A. E. Martell, R. J. Motekaitis, and D. McManus, *Can. J. Chem.*, **76,** 445 (1998).

[8] J. M. Scanlon, E. Aizenman, and I. J. Reynolds, *Eur. J. Pharm.*, **326,** 67 (1997).

[9] P. M Jackson, C. J. Moody, and R. J Mortimer, *J. Chem. Soc., Perkin Trans.* 1, **12,** 2941 (1991).

[10] L. F. R. Cafferata and C. W. Jefford, *Molecules*, **6,** 699 (2001).

[11] S. Burkhardt, R. J. Reiter, D. X. Tan, R. Hardeland, J. Cabrera, and M. Karbownik, *Int. J. Biochem. Cell Biol.*, **33,** 775 (2001).

[12] W. M. H. Behan, M. McDonald, L. G. Darlington, and T. W. Stone, *British J. Pharmacology*, **128,** 1754 (1999).

[13] H. L. Campbell and B. A. Striebig, *Environ. Sci. Technol.*, **33,** 1926 (1999).

[14] H. W. Rich, K. Hegetschweiler, H. M. Streit, I. Erni, and W. Schneider, *Inorg. Chim. Acta*, **187,** 9 (1991).

[15] Y. Yokoi, T. Mori, T. Mitani, and S. Kawate, *Bull. Chem. Soc. Jpn.*, **65,** 1898 (1992).

[16] D. Chen, A. E. Martell, R. J. Motekaitis, S. Niu, and D. McManus, *Inorg. Chim. Acta*, **293,** 206 (1999).